Facile Synthesis of Useful Carboxylic Acids
by Electrochemical Carboxylation

Masao Tokuda, Daijiro Furuya, Hirokazu Komatsu, Hirotaka Kanaya, Nobuhito Kurono, and Hisanori Senboku

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Electrochemical fixation of carbon dioxide is a useful and attractive method for efficient synthesis of various carboxylic acids. We previously reported that electrochemical carboxylation of allylic and propargylic halides, vinyl bromides, vinyl triflates, and phenyl-substituted alkenes proceeded efficiently to give the corresponding carboxylic acids in high yields when a magnesium metal was used as a sacrificial anode. In this paper, we report facile synthesis of arenedicarboxylic acids and cyclic [2]-alkoxyl- or cyclic [2]-amino-[1,2]-unsaturated carboxylic acids by electrochemical carboxylation of polyaromatic compounds and lactone or lactam enol triflates.

Synthesis of Arenedicarboxylic Acids

Electrochemical carboxylation of naphthalene in acetoniitrile containing 0.1M Et$_3$NClO$_4$ with a Pt cathode and a Zn anode under an atmospheric pressure of carbon dioxide gave two dicarboxylic acids 1 and 2 in 89% and 11% yields, respectively. When this electrolysis was carried out in supercritical carbon dioxide (scCO$_2$, 40 °C, 7.5 MPa), acids 1, 2, and 3 were obtained in 53, 29, and 18% yields (Scheme 1). On the other hand, dicarboxylic acids 4 and 5 were obtained in high yields as a single product by similar electrochemical carboxylation of anthracene and phenanthrene, respectively (Scheme 2). Electrolysis of anthracene under supercritical conditions of carbon dioxide (scCO$_2$) gave 4 in 87% yield, although the similar electrolysis in acetoniitrile solution in the presence of atmospheric CO$_2$ gave a lower yield of 4 due to low solubility of anthracene in acetoniitrile. Other results will also be reported.

Synthesis of Captodative Cycloalkenes

Lactone or lactam enol triflates 6 were readily prepared from the corresponding lactone or lactam. Electrochemical carboxylation of lactone enol triflates (6) in DMF containing 20 mol% of NiBr$_2$, bpy with a Pt cathode and Mg anode under an atmospheric pressure of CO$_2$ gave cyclic [2]-alkoxyl-[1,2]-unsaturated acids (7), captodative cycloalkene, in good yields (Scheme 3). These alkenes are useful as synthetic intermediates. Various cyclic [2]-alkoxyl-[1,2]-unsaturated acids 8-15 and cyclic [2]-amino-[1,2]-unsaturated acid 16 were obtained in the yields shown in Scheme 4. In the case of 15, electrolysis in the absence of Ni catalyst gave a higher yield (82%) of the product.

REFERENCES